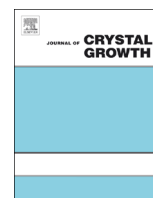




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journal homepage: www.elsevier.com/locate/jcrysgrInvestigation of thermodynamics properties of chalcopyrite compound CdGeAs₂

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ABSTRACT

Chalcopyrite of CdGeAs₂ single crystal was grown by a modified vertical Bridgman method with sufficient size and quality, and its optical, electrical and thermodynamic properties are characterized. The transmission is recorded in the 2.3–18 μm range, and the band-gap at room temperature is at 0.56 eV. Non-ideal transparency near 5.5 μm which limited its application severely exists in the front of the crystal. The crystal is *p* type at room temperature with hole concentrations varying from 10¹⁴ to 10¹⁶ cm⁻³. From the results of X-ray diffraction measurements carried out over the range 25–450 °C and thermal dilatometer tests, the thermal expansion coefficients are evaluated. And on this basis the Grüneisen parameters at different temperatures are evaluated and also exhibit anisotropic behavior ($\gamma_a > \gamma_c$). It is found that γ_a , γ_c , and γ_V have some difference between these two kinds of test methods. Using these Grüneisen parameters, lattice thermal conductivities have been deduced by two correction formulas. Meanwhile, specific heat capacity and thermal conductivity of [204] have been obtained as a function of temperature by experiment.

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1. Introduction

Ternary compounds with chalcopyrite structure, which were first discovered by Hahn et al. [1] in 1953, have received a great of attentions because of their applications in optical devices, detectors and solar cells [2,3]. Cadmium germanium arsenide (CdGeAs₂) is an ideal candidate material for nonlinear optical (NLO) applications, since it has the highest NLO coefficient ($d_{36}=236$ pm/V) [4,5]. Its wide transparency range (2.3–18 μm), accompanying by significant birefringence, makes this material very promising in frequency conversion applications in the infrared range [6].

Since the 70s, researchers have struggled to grow large and high quality single crystals of this compound, but they were plagued by polycrystallinity and cracking [7–13] due to highly anisotropic thermal expansion coefficients [14]. Therefore, the investigation of anisotropic thermal expansion coefficients has great significance for the improvement of the CdGeAs₂ crystal growth. Newmann [15] and Kumar et al. [16] have evaluated the average linear thermal expansion coefficient α_l based respectively on empirical and modified empirical relation from first principles. Kildal [17] and Kozhina et al. [18] reported the experimental

average thermal expansion coefficients in two main directions (namely, α_a and α_c) in the range 100–300 °C and 20–400 °C, respectively. However, in many cases, the results seem inadequate in practice, and it is expected to reveal thermal expansion mechanism in specific directions and at specific temperatures which is conducive to the crystal growth. With the development of horizontal gradient freeze method [19,20] and modified vertical Bridgman method [21,22], single crystals of this ternary chalcopyrite have been grown without severe cracking. Meanwhile, up to now, structural [10,23,24], electronic [2,25] and optical properties [6,8,26] of CdGeAs₂ have been studied for the last four decades by a number of experimental and theoretical methods. However, the thermal conductivity of the I–III–VI₂ or II–VI–V₂ chalcopyrite crystal, which is an important thermodynamic parameters in the aspect of laser application, were usually discussed at ambient temperature or under ambient temperature in the literature, and the derivation formulas of thermal conductivity were different [27–30] each other. To achieve high power laser output, the investigation of the thermal conductivity is indispensable.

Herein, we address the interesting about the CdGeAs₂ crystal growth by the modified VB method as well as optical, electrical and thermodynamics characterization, and have deeply discussed the properties of anisotropic thermal expansion, heat capacity and thermal conductivity.

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2. Experimental section

2.1. Crystal growth

The starting material was synthesized from high purity 6 N Cd spheroids, 6 N Ge and 6 N As lumps about 120 g at the molar ratio of 1:1.005:2.01. After weighing in a glove box, the charges were loaded into a quartz ampoule and sealed under 10^{-5} Pa at once. Then the ampoule was put into a rotatable tube furnace and the synthesis was mainly carried out with such steps: 50 °C/h to 650 °C, 8-h soak and 20 °C/h to 950 °C, 24-h soak. In order to make the raw materials mix uniformly and drive the residual Cd and As vapor out of melt, the furnace rotating and the temperature oscillation (between 800 and 1040 °C) have been carried out several times [31,32]. When the synthesis process finished, the furnace were cooled down to room temperature at the speed of 20 °C/h.

The polycrystalline material was taken out of the synthesis ampoule and ground into powder. Meanwhile, the polycrystalline XRD and EDS analysis demonstrated that there is no impurity phases in the powder. Then the polycrystalline powder was reloaded into a carbon-coated quartz ampoules. After being evacuated to 10^{-5} Pa, the polycrystalline powder was sealed into the quartz ampoule. Then the quartz ampoule was placed into a three-zone furnace. The temperatures of the upper, middle and lower zones were raised to the special temperatures at the rate of 12 °C/min, respectively. After a lot of growth runs, we find that if the temperature of the upper zone is higher than 720 °C, the obtained products are most polycrystal. But if the temperature of the upper zone is too low, the appropriate temperature gradients is hard to achieve. A suitable temperature gradient not only can provide a sufficient nucleation driving force, but also restrain the formation of polycrystalline boules. Therefore, we have carried out a lot of growth runs with the temperature gradients of 10–35 °C. At last, temperature gradients of 15–25 °C/cm are adopted, which is different from the small temperature gradients (1–3 °C/cm) in the horizontal gradient freeze method [20] and is smaller than that reported in the early vertical Bridgman method (40 °C/cm) [9]. The growth position of the ampoule was adjusted to the place where the indication of the monitoring thermocouple was about 670 °C. The entire charge was heated above the melting point. Over 100 °C of supercooling (down to 547 °C) took place before the onset of crystallization [20]. So when the material in the seed well solidified, the ampoule was pulled back to the position where the temperature is about 650 °C. Then the material in the seed well was reheated to partially melt back and the growth ampoule was mechanically descended at the rate of 0.21–0.25 mm/h. After the growth process finished, the temperature was cooled down to room temperature at 20 °C/h. Thus, CdGeAs₂ single crystals could be obtained reproducibly, which is shown in Fig. 1.

2.2. Characterization

The optical transmittance spectra of as-grown CdGeAs₂ wafers were recorded using a Shimadzu fourier-transform-infrared (FTIR) spectrometer in the range of 2.3–18 μm. The samples are approximately 2 mm thick which were polished smoothly. Electrical properties were obtained using Ecopia HMS-300 Hall-effect measurement system. Temperature could be controlled at 77 and 300 K, and the measurements were carried out at a magnetic field of 0.554 T. A circular diamond saw was used to cut the as-grown bulk crystal, verifying the orientation of the surface by XRD. The CdGeAs₂ crystals were carefully examined by the powder XRD (DX-2000, Dandong, China) method at room temperature. The diffraction patterns were recorded over the 2θ range of 10–90°. The high-temperature XRD measurements were performed in a

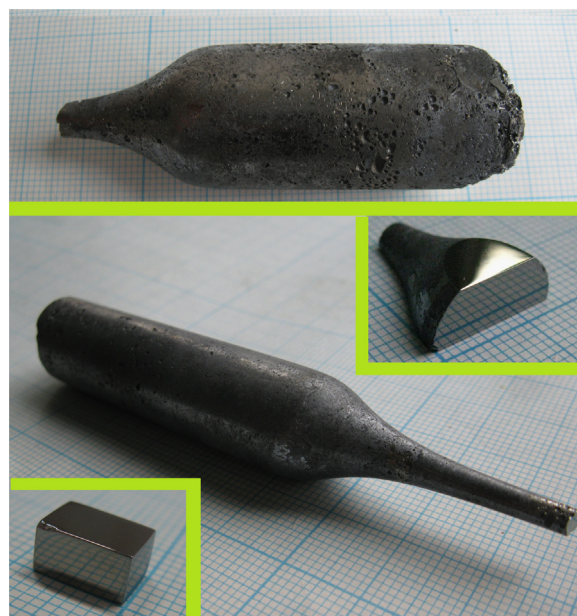


Fig. 1. Photograph of crack-free CdGeAs₂ single crystals and an embryo of SHG device.

DX-2700 diffractometer with Cu K α radiation, and Graphite monochromator was adopted to select single wavelength of about 1.54 Å. The temperature stages for X-ray diffraction measurements were determined at 25, 100, 200, 300, 400, and 450 °C, respectively. Prior to thermal conductivities measurements, a series of thermogravimetry and differential scanning calorimetry (TG-DSC) measurements in the shielding nitrogen ambient were carried out in a SDT Q600 apparatus (TA Instruments, USA) for heat capacity, and the sample size is $\Phi 5$ mm \times 1 mm. After careful calibration of the calorimeter and using Al₂O₃, as standard the heat capacities could be measured with a high-accuracy. Thermal conductivities were determined at 26.6, 100.6, 200.4, 300.4 and 400.3 °C by NETZSCH LFA 457 which adopt the InSb detector and Ar protective atmosphere with 50.00 ml/min. The diameter and thickness of test sample were 12.7 mm and 1.8 mm, respectively. Due to the size limitation, thermal conductivity experimental only with [204] direction could be obtained. The [204] direction is just the growth direction in this VB method so that the sample has a large enough diameter.

3. Results and discussion

3.1. Optical and electrical properties

The IR transmittance of a CdGeAs₂ wafer is shown in Fig. 2 and the maximum value is up to 51.6% in the range of 2.3–18 μm. Absorption coefficients (α) were estimated from the transmission spectrum of CdGeAs₂ single crystals. The inset shows the value of $(\alpha h\nu)^2$ vs photon energy at room temperature. The useful transmission range is limited by the strong absorption below 2.3 μm due to transitions across the band-gap and by two-phonon absorption at 12.5 and 13.5 μm, which are present in all of samples, are probably due to three-phonon processes. The absorption coefficients at 5.5 μm is close to the lowest optical losses (0.18 cm^{-1}) measured by K. Nagashio [33]. The broad band peaking near 5.5 μm has been ascribed to transitions between a split-off valence band and the highest valence band at $k=0$ [2]. Since the EPR hyperfine interactions suggested the acceptor was located on the As site. Lihua Bai [34] believed the shallow acceptor was a

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